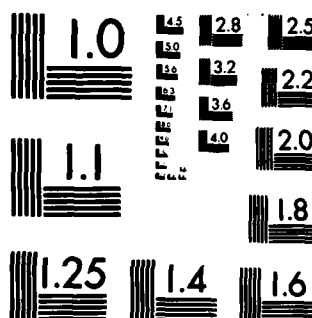END

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SYNTHESIS OF HYDROPHOBIC, CROSSLINKABLE RESINS

FIRST ANNUAL REPORT

by

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THE SYNTHESIS OF HYDROPHOBIC, CROSSLINKABLE RESINS

SUMMARY

This project is concerned with new methods of synthesizing thermosetting resins. The resins to be produced are intended as matrix materials for fiber composites, and other organic products such as adhesives. The resins must have good moisture resistance. That is, the materials must withstand prolonged use under conditions such as $80°C$ and 95% relative humidity, with good retention of mechanical properties in the dry state at up to $125°C$. The fabrication procedures should be comparable in simplicity with those currently in use in the industry.

The report discusses the approaches available, and covers the literature from 1974 to 1983. The literature discussed is mainly that concerning reactions with potential (a) in producing prepolymers and (b) in subsequently carrying out free radical crosslinking reactions. Literature relating to established thermosetting resins, and to novel resins which do not promise hygrothermal stability, is excluded.

Brief indications are given of some experimental procedures currently under investigation. The common feature of these procedures is that they utilise the Wittig reaction for producing crosslinking sites. Originator Furnished Keywords include:

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SYNTHESIS OF HYDROPHOBIC CROSSLINKABLE RESINS

Contract Number DAJA 45-84-C-0016

1.INTRODUCTION

A large number of reinforced plastics products to-day are made from crosslinked, i.e. thermosetting matrix resins.This is especially true of high performance aerospace composites. However, there is increasing competition from thermoplastics, which offer the advantages of improved damage tolerance, or toughness, and improved moisture resistance. An example of the thermoplastics materials currently being offered for use in high performance composites is "PEEK", or polyether-ether ketone made by ICI. Its advantages derive chiefly from its semi-crystalline structure, which imparts the ability to absorb energy and to make the entry of water molecules by activated diffusion extremely difficult.

It is by no means certain whether thermosetting resins have yet achieved their optimum performance. This project is concerned with developing improved thermosetting resins of low water resistance. Thermosetting resins have many advantages in composite applications, particularly in their ease of impregnating fibers. They also have high glass transition temperatures; most of the thermoplastics materials are not recommended for use at temperatures above about 125^0C because of loss of mechanical properties.

Almost all the main thermosetting resins in large scale production to-day were first envisaged at least forty years ago. There have been many new developments in synthetic organic chemistry since then, but the exploitation of these innovations in resin technology has largely failed for various practical reasons. Nevertheless, it should be possible to utilise some of these novel reactions in producing polymers which are largely free of hydrophilic groups such as ester, hydroxyl, carbonyl or amine. Such polymers should have low diffusivities and low equilibrium water absorption levels. Therefore they should resist hygrothermal degradation processes, whether physical or chemical, which cause lowering of modulus and Tg,

hydrolysis, internal cracking, leaching etc. Unsaturated polyesters are notoriously prone to degradation by hot water, and undergo hydrolysis of the ester groups. Epoxy resins have relatively low water absorptions and do not usually have any ester groups to encourage chemical degradation, but they can undergo substantial deterioration from other causes, notably internal cracking. Phenolic resins are adversely affected by the large number of hydroxyl groups.

There are many hydrophobic polymers already, but they are not suitable for use in fiber resin composites. Two examples are the synthetic rubbers such as polybutadiene, which have no main-chain stiffening groups and therefore have unacceptably low moduli at ambient temperatures, and crosslinked polystyrene, which is unsuitable for fiber impregnation and does not possess good thermomechanical properties. Our assumption is that a suitable material should have a structure of the following kind:

(1) It should be largely hydrocarbon, since other means of moderating the hydrophilic character such as fluorination are expensive

(2) There should be a pre-polymer of low molecular weight (Mn = 300 to 2000) which can be converted to a network polymer by a subsequent reaction during the molding operation

(3) The prepolymer should have stiffening groups, e.g. mainchain benzene rings, in it, but it should also have some flexibility, imparted by linkages with low rotational energy barriers.

(4) The crosslinking reaction should not introduce hydrophilic groups

(5) The crosslinking reaction should not produce volatiles which cause void formation.

(5) There should be no water-soluble residues in the final product.

The main part of this report (section 2) deals with the recent literature relating to potential new methods of making network polymers of a generally hydrophobic character. The last part describes preliminary experimentation to evaluate one or two specific approaches to the problem.

2.LITERATURE SURVEY.

2.1.Scope.

The survey describes attempts to produce novel crosslinkable polymers or thermosetting resins, as reported in the open literature between January 1974 and December 1983. The size of this task has been greatly reduced by eliminating references to minor variants on existing,

established thermosetting systems such as phenolic, amino, polyester, and epoxy resins. Also,there is no discussion of novel thermosetting resins unless they appear to have potential as hydrophobic materials, or the method used has wider application and could be suitably adapted. Some methods have been ruled out because of their dependence on exotic, expensive, or otherwise undesirable reagents.

Attention is also directed to untried but feasible procedures, such as the synthesis of suitable prepolymers, having the characteristics described in section 1, and the modification of saturated prepolymers to form suitable structures.

Lastly the discussion narrows to focus specifically on our proposed routes. It will be noted that at this stage the only procedures considered are those involving free radical crosslinking, since (a) the technology for effecting it is established, (b) there are no volatiles to produce voids in moldings and (c),there is no need for high pressures. The possibilities are restricted by the fact that several all hydrocarbon double bond systems do not readily undergo free radical crosslinking reactions. Examples are propene and various allylic monomers.

2.2. Novel Crosslinkable Systems.
### Crosslinking via double bonds.

An important development was that of the polystyryl pyridine <PSP> resins announced by Ropars and Bloch [1]. These are formed by the condensation of methyl substituted pyridines with aromatic dialdehydes to form alternating chains of aromatic and heterocyclic rings, linked by double bonds which can be crosslinked thermally [see Fig.1].

Another group to receive much attention was the family of hydrophobic bis-diene resins, formed by end capping active chlorine terminated molecules with cyclopentadienyl sodium. These react further to give oligomers containing dicyclopentadienyl nuclei, which on heating to 200°C split out cyclopentadienyl radicals.These then react with unchanged oligomer to form three dimensional structures [2].

Many oligomers have been end capped with cyclopentadienyl type groups,for example the P13N resin developed by TRW Systems [3], which is a polyamic acid terminated by norbornylene groups. On heating, a maleimide type prepolymer and cyclopentadiene are formed which thermally crosslink. Bismaleimides have also been crosslinked with radical initiators to produce brittle networks [4].If a diamine is added, chain extension and radical crosslinking both occur to produce a more useful structure [5].

Other developments in this area include the

FIG. 1

POLYSTYRYL PYRIDINE RESINS (1)
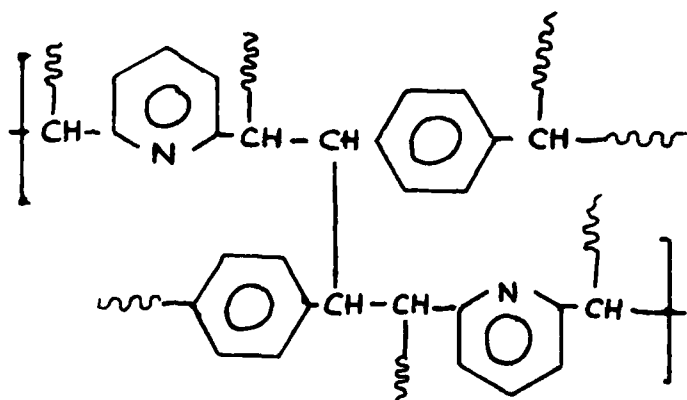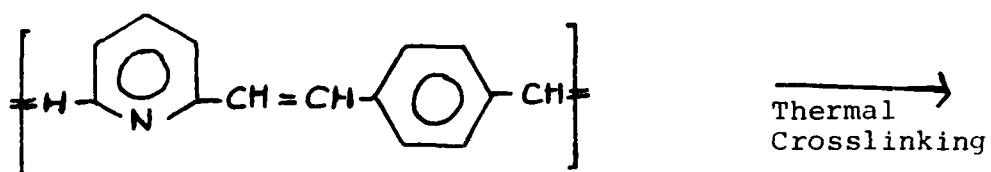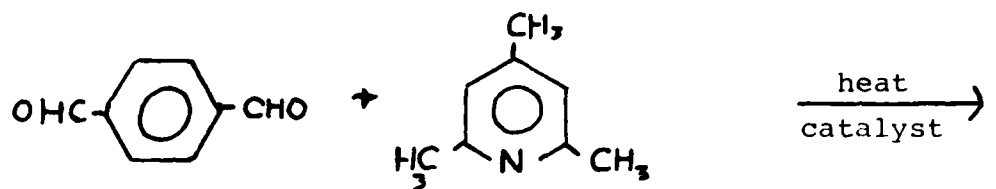
production of heat resistant polymers with main chain
olefinic unsaturation (conjugated C=O and C=C bonds) [6]
and polyethers containing pendant unsaturated ester groups
[7].

Crivello and Conlon [8] have reported the use of
aromatic bisvinyl ethers (formed by the reaction of
bisphenols with 2-chloroethyl vinyl ether) as thermosets.
These are crosslinked by cationic initiators such as
diaryliodonium salts to form structures similar to epoxy
resins.

There have been relatively few thermosets with
styrene type unsaturation, possibly because of the difficulty
in preparing such systems, and the high reactivity of these
double bonds with radicals, cations and anions.

A prepolymer, consisting of a phenyl quinoxaline
oligomer end capped with divinyl benzil has been reported
[9]. This was prepared by reacting a bis <3,4,diamino>
quinoxaline system with divinyl benzil to form a chain with
two terminal olefinic groups at each end. Crosslinking was
via free radical reactions (see Fig.2).

In this laboratory a thermosetting resin was
produced from the Friedel Crafts reaction of stilbene with
p-dimethoxyxylene [10]. This was crosslinked with maleic
anhydride to produce a three dimensional structure.

The network copolymerisation of bis <p-vinyl
phenyl alkanes >with styrene has also been reported in the
literature [11].

Crosslinking via triple bonds.

At high temperatures, polymers containing
acetylenic or nitrile groups have been found to produce
crosslinked structures. Originally, this was thought to occur
via cyclisation reactions, but now intermolecular addition
reactions are thought to be more important [12].

Considerable research has taken place in this
field and a wide rangeof high temperature resistant oligomer
systems have been developed. Acetylene terminated oligomers
include benzene derivatives [13], polyphenylquinoxalines
[14-15], polyimides [16], and various
polyether-ketone/sulphone systems [17-20].

Among nitrile containing oligomers are the
polyarylene sulphides [21], the polyphenylenes [22],and the
polyether sulphones [23]. All of the above systems require
high temperature curing.

Acetylene terminated polymers have been produced
commercially. These include acetylene terminated
polyphenylenes (H Resins) [24] and polyimides (HR Resins)
[25]

FIG. 2

DIVINYLBENZIL END CAPPED PHENYLQUINOXALINE OLIGOMER (9)
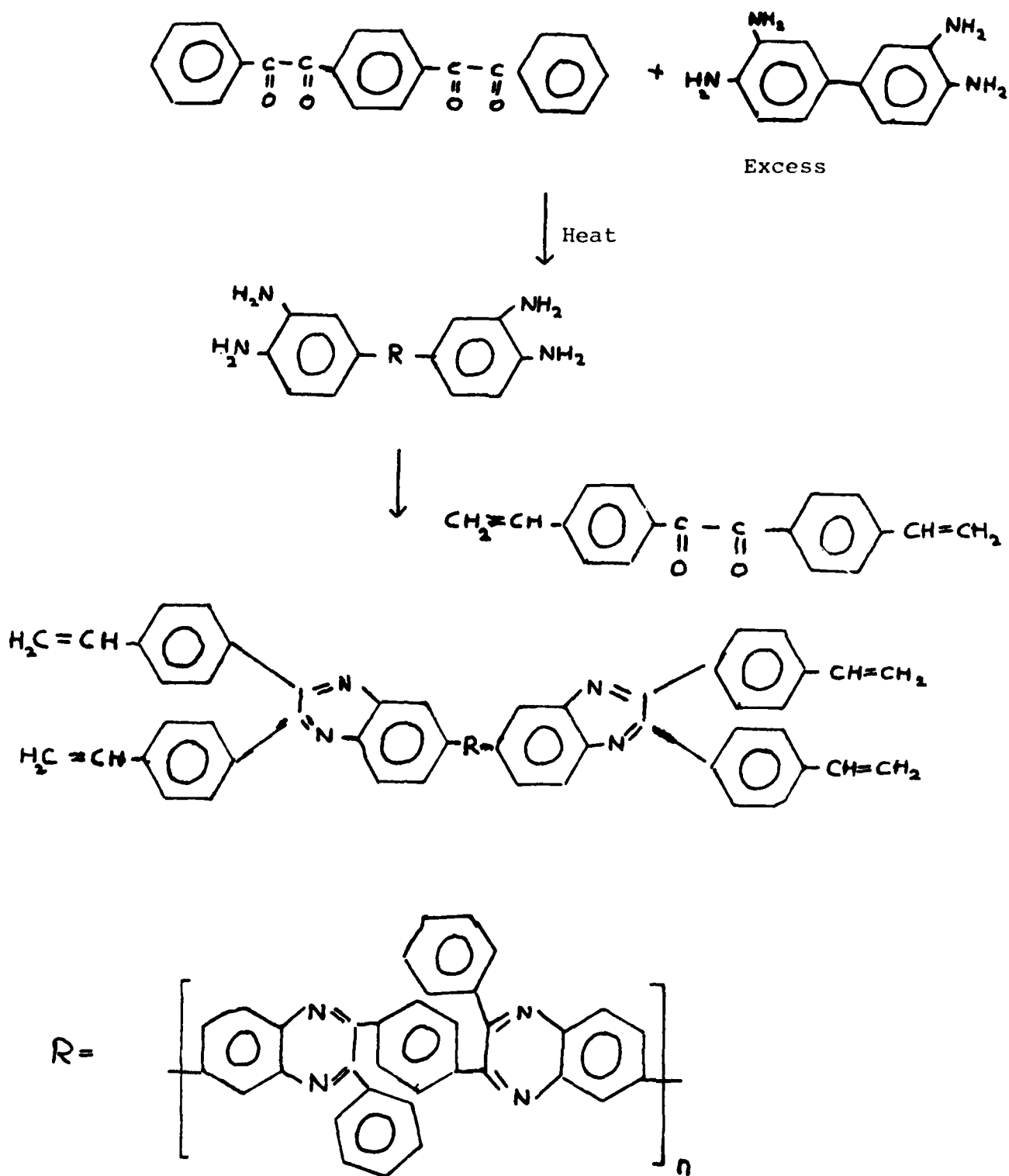
Crosslinking by other means.

A variety of other ways of producing crosslinked polymers have been reported - many of these suffer disadvantages caused by the release of volatile or water soluble materials during cure, or require exotic groups as the crosslinking center.

Monsanto [26] produced a laminating resin of the polyphenylene type by the reaction of benzene 1,3,disulphonyl chloride with various terphenyls.The soluble prepolymer could be reacted with more of the sulphonyl chloride to introduce crosslinking, but sulphur dioxide and HCl are produced during cure.The company also produced a similar phenylene based resin, with pendant nitrile groups which could be crosslinked without the evolution of volatiles [18].

ICI has developed a thermosetting resin from a dihalobenzenoid compound, a double alkali metal salt of a bisphenol and a polyhaloheterocycle. The curing reaction produces sodium chloride [27].

Du Pont [28] produced a thermoset from a bisphenol and perhalogenated aromatic compound that crosslinks in a similar manner to the ICI thermoset mentioned above.

Albright and Wilson [29] patented a novolak type polyphenylene produced from benzene 1,3,disulphonyl chloride and phenol, which could be crosslinked with hexamethylene tetramine. Similar polymers have been prepared by polymerization of phenyl allyl ether. Rearrangement occurs during the polymerisation step to produce a hydroxy substituted polymer, which can be crosslinked with hexamethylene tetramine [30].

The UK MOD have obtained a patent for a Friedel Crafts crosslinked polymer derived from toluene and p-xylylene glycol dimethyl ether [31] which evolves methanol on cure.

In the Soviet Union, Korshak et al reported the preparation of soluble branched polyphenylenes, formed from 4,4´,diacetyl diphenyl ethyl ketal and a monoethyl ketal with HCl. On heating, these produced an insoluble structure with the evolution of ethanol [32].

Another approach to thermosets has been the use of soluble polymers with groups which rearrange on heating to give insoluble products, in reactions analogous to the preparation of polyimides from polyamic acids. Examples from the recent literature are provided by the enyne polysulphones, which rearrange on heating to give naphthalene residues on the polymer backbone [33] and polymers containing 2,2´,diphenyl ethynyl 4,4´,diphenyl units, which rearrange to give polycyclic structures [34]. (Fig.3)

Amongst novel curing methods are the incorporation

FIG. 3

REARRANGEMENT OF 2,2' DIPHENYLETHYNYL 4,4' DIPHENYL UNITS (34)
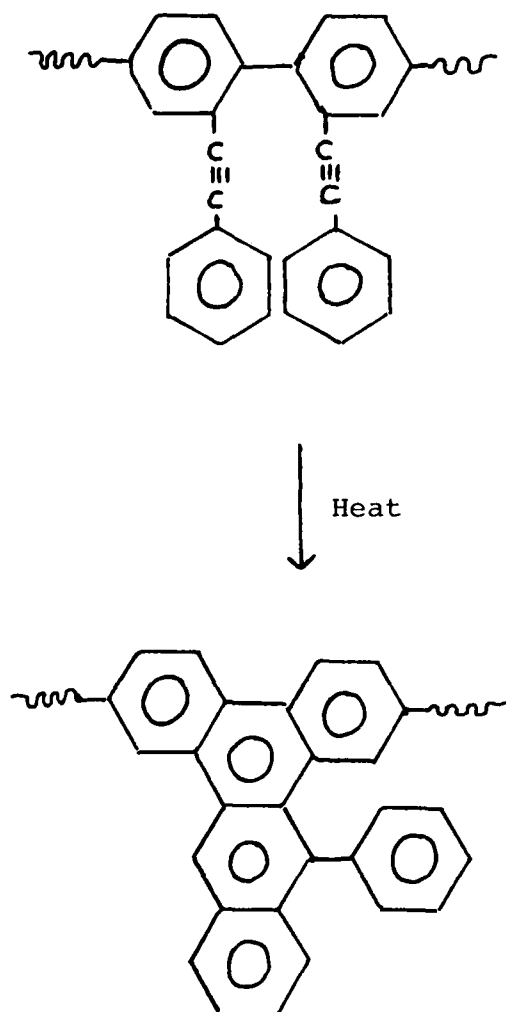
of biphenylene [35] or aryl disulphide [36] units in the
polymer backbone - these are thermally unstable, and high
cure temperatures lead to radical crosslinking via the
opening of strained rings.

2.3.Synthesis of unsaturated prepolymers.
This section is concerned with methods of producing
prepolymers, i.e. linear polymers, which already contain
unsaturated groups suitable for crosslinking by free radical
methods. It deals mainly with the potential utility of the
Wittig reaction in prepolymer synthesis, and with the
associated problem of obtaining suitable monomers for Wittig
polymerization.
        The Wittig reaction has been used extensively in
synthetic organic chemistry for the preparation of alkenes,
generally in high yields [37].
        The reaction was first applied to polymer
synthesis by McDonald and Campbell in 1960. Two approaches
were adopted, one involving the reaction of a diphosphonium
salt with a dialdehyde, and the other the reaction of a
compound containing both functional groups [38]. (Fig.4)
        The first approach, using dichloro-p-xylene and
terephthaldicarboxaldehyde, produced an intense yellow
coloured, insoluble polymer, with a number-average molecular
weight (Mn) of about 1200.
        The second approach involved the Wittig
polymerisation of 2,methoxy,5,methylal benzyl chloride
(formed by the chloromethylation of anisaldehyde) which
yielded a soluble colourless polymer with terminal
carboxaldehyde groups.
        Experimental work in this laboratory has produced
a yellow coloured, soluble polymer by the reaction of
mixtures of meta and para dichloroxylene with
terephthaldicarboxaldehyde via the Wittig reaction. The use
of mixed isomers is important for subsequent processing
purposes.   When the highly unsaturated polymer was
crosslinked with styrene and benzoyl peroxide at 100°C a
hard, brittle, insoluble material was formed.
        There are two possible ways of altering the
properties of the above product. One is to partially
hydrogenate the polymer in order to reduce the crosslink
density, and the other, more promising approach is to modify
the starting materials. Both the reagents in the above
synthesis are relatively expensive, so cheaper materials are
necessary and, if suitably chosen, they will also reduce the
density of double bonds and introduce flexibilising groups.
The main approaches to producing new starting materials are:

FIG. 4

WITTIG POLYMERS AS PREPARED BY McDONALD AND CAMPBELL (38)
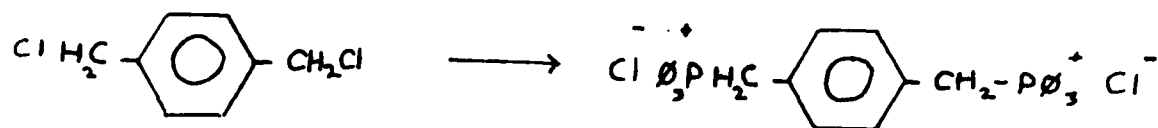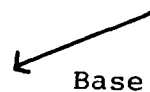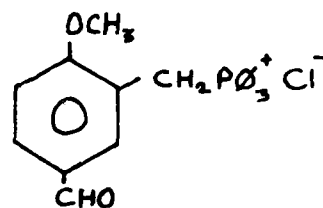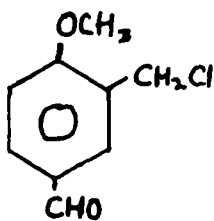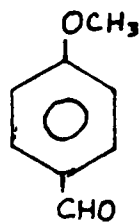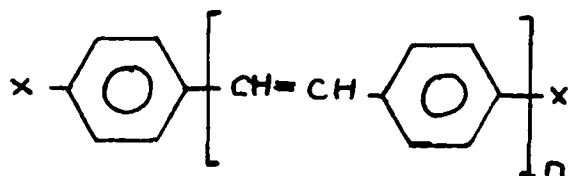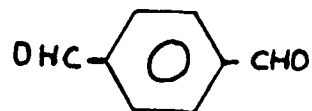
1.Chloromethylation.

The classical method of chloromethylation [39] used to involve formaldehyde, HCl and a Friedel Crafts catalyst but this procedure is now no longer used, as bis <chloromethyl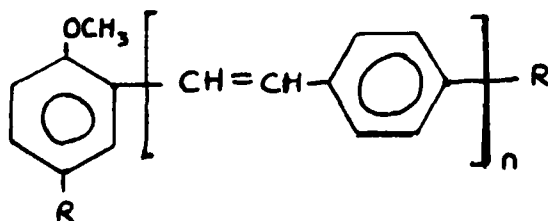> ether, a potent carcinogen, is a by-product . Chloromethyl methyl ethers [40] are much less potent carcinogens. However, the commercial product is contaminated with the bis <chloromethyl> ether.

A new synthesis has been developed, which avoids the problem of contamination and produces the ether in near quantitative yield [41]. There are also chloromethylating reagents such as 1,4,bis <chloromethoxy>butane and 1,chloromethoxy 4,chlorobutane [42], which have lower vapour pressures and therefore reduce substantially the risk of exposure to these potential carcinogens. Diphenyl ether is a suitable substrate for chloromethylation, as it contains activated nuclei. The reaction has been used to chloromethylate polyether sulphones in high yield for the production of ion exchange resins [43].

2.Chlorination.

Aromatic substrates with pendant methyl groups can readily and selectively be halogenated by a variety of reagents, with formation of the benzyl radical. Reagents include:

a.N Bromosuccinimide / peroxide. This system is expensive.
b.Chlorine / peroxide.
c.Bromine / peroxide. (Bromine is a more expensive but more selective reagent than chlorine.)
d.Sulphuryl chloride / peroxide. This is a cheap and effective method for benzylic chlorination. It has been patented by Rohm and Haas as a method of producing ion exchange resins from polymers of p-methyl styrene [44].
e. Chlorine / phosphorus pentachloride / peroxide.

3.Formylation.

Amongst the methods available for formylation are :
a.The Gatterman-Koch reaction [45] (Unsuitable for phenyl ethers because of complex formation.)
b. The Gatterman Formylation [46] using zinc cyanide, hydrogen chloride and aluminium trichloride.
c. The Vilsmeyer formylation,using a secondary amine with formic acid and phosphorous oxychloride [47].
d. Probably the most convenient method utilises dichloromethyl methyl ether with a Friedel Crafts catalyst [48]. This can be applied to a number of compounds, and

yields are generally high.

A review of the above methods and their use in the functional modification of polystyrenes is available [49].

4.Friedel Crafts reactions.

There is scope for the synthesis of new monomers by means of Friedel Crafts reactions. One approach is a modification of the work of Bachmann and Hellman [50], involving alkylation with propylene chlorohydrin.

5.Grignard Reactions.

Another possible route to Wittig monomers is the reaction of di-Grignard reagents with epoxides, to form diols which can be converted to the dihalo compounds by reagents such as thionyl chloride.

Wittig polymers, similar to those produced in this laboratory, have been produced commercially. One of the patents concerned their use as electrical conduction systems [51] and the other related to the electrical properties of high molecular weight compounds with conjugated structural arrangements [52].

A variety of other methods may be available to incorporate unsaturation during the polymerisation step.

The production of xylylidene polymers, similar to those produced by the Wittig reaction, has been accomplished by the base catalysed condensation of dichloro-p-xylene. Bases include sodium amide in liquid ammonia [53], and hydroxide ion under phase transfer conditions [54].

Alternative methods for the direct production of unsaturated prepolymers have a number of problems:

a.Trifunctional unsaturated intermediates may be required (e.g. for polycondensation reactions) which are either difficult or extremely expensive to produce.

b. Unsaturated compounds such as styrene react with Lewis acids and so the scope for Friedel Crafts reactions is limited. Stilbene and its derivatives may be employed in such reactions.

c.The choice of double bond system is extremely limited by the stipulation that the bonds must be reactive to free radical polymerisation, and must not be associated with hydrophilic groups.

2.4.Saturated Prepolymers.

There are many polymer structures which do not possess obvious reactive sites, such as unsaturated groups, for crosslinking, yet which otherwise possess suitable chemical structures for incorporation into a hydrophobic resin system. This section considers some of the prepolymers which could, after suitable functionalisation by methods such as those described in sections 2.3 and 2.5, be converted into crosslinked polymers. No account has been taken at this stage of the need to control the molecular weight of the prepolymers, which must be low enough to facilitate fiber impregnation and moulding operations.

Aromatic Polyethers and polysulphides.

These systems are of interest because they contain aromatic rings linked directly by flexibilising units, and have some hydrophobic character. They are therefore potentially useful backbones for chemical modification. Polyethers and polysulphides are activated towards electrophilic substitution reactions. They have been produced with varied alkyl substituents, and oligomers with terminal halogen atoms have been reported, making them suitable candidates for such modifications.

The main route to polyethers is that developed by GEC for its Noryl range [55]. Ethers are produced by oxidative coupling of various methyl substituted phenols with copper complexes. Substituents vary, but include methyl, dimethyl and halo derivatives. 2,6,diprenylphenol (where prenyl= 3-methyl, 2-butenyl) has been oxidatively polymerised with retention of unsaturation [56].

Amongst the alternative syntheses are:

1. The reaction of an alkali metal diphenolate with a dihalodiphenyl compound in diphenyl ether [57].

2. Polymerisation of p-chloro potassium phenolate [58].

3. Nitro displacement reactions [59]. For example a nitrile substituted polymer is produced from the reaction of Bisphenol A with 2,6,dinitro phenyl cyanide.

The main route to polysulphides is that patented by Phillips Petroleum [60]. It involves the reaction of dihalo aromatic compounds with dehydrated sodium sulphide in a high boiling solvent. A range of products have been reported:

a. Polyphenylene / poly 2-methylphenylene / poly 2,6,dimethylphenylenesulphides [61].

b. Polyphenylene sulphide oligomers terminated by bromo,

cyano, methyl, hydroxyl groups etc. [62].
  c. Polychloro diphenyls [63].
  d. Polyphenylene sulphide sulphones [64].
  e. Co-oligophenylene sulphides [65].
          Other methods for their synthesis include:
  a. The preparation of oligoarylene sulphides by a trans
arylation reaction [66].
  b. Phase transfer catalysed nucleophilic displacement
reactions, e.g. from bis [4,chloro,3,nitrophenyl] sulphone
and 4,4'oxydibenzenethiol [67].
  c. Preparation of polyhydroxyphenylene sulphides from
sulphur and phenols by activation with halogens [68].
          Aralkyl polyethers and polysulphides.
          Polyethers of high molecular weight have been
produced by polycondensation of diphenolic compounds with
aromatic dichloromethyl compounds. The process has been
patented by Kaufman [66] and involves coupling reactions at
high temperatures by potassium carbonate in DMA. Other
similar reactions have been reported [70-71] and the
generation of such systems is considered further in the
section on phase transfer catalysis.
          Amongst methods for the production of aralkyl
sulphides are:
  a. Addition of dithiols to divinyl compounds having nitro or
cyano groups as beta substituents [72].
  b. Phase transfer reactions (see below)
                      c.Ring opening reactions of cyclic
sulphides [73].
          Phase transfer catalysis.
          Over recent years there has been considerable
interest in phase transfer catalysis as a novel
polymerisation method, and as a means of polymer
modification. The method utilises phase transfer catalysts
such as tertiary ammonium salts, and crown ethers with
aqueous base and an immiscible organic solvent.
          A variety of polymer systems have been prepared by
this method, including polycarbonates [74], polysulphonates
[75], polyesters [76], polyethersulphones [77], polysulphides
[78] and polyethers [79-81].
          Polyethers with main chain aromatic rings are of
particular interest. N'Guyen and Boileau [79] reported the
synthesis of a polyether from bisphenol A and
dichloro-p-xylene, as did Cameron and Law [80]. The ether, of
molecular weight [Mn] c4000, was only partially soluble in
dimethyl sulphoxide and was considered to be contaminated
with xylylidene units in the backbone.
          The system was refined by Imai and Yamazaki [81] so
as to produce completely soluble polymers of high molecular
weight (as defined by viscosity measurements).

An attempt has been made to modify the above system to produce low molecular weight oligomers terminated by chloromethyl groups - this approach has had some success, and low molecular weight chloromethyl terminated oligomers have been produced which are soluble in solvents such as chloroform. As yet, the yields have not been optimised, but the Wittig reaction with formaldehyde has shown promising results.

Also in the N´Guyen and Boileau paper was the production of polyethers from bisphenol A and 1,4 dichlorobut-2-ene. Similar polymers have been produced in this laboratory, but as could be expected, the unsaturated groups are not reactive towards free radicals. Problems were also experienced with the purity of the commercially available product.

Polymers prepared from organometallic reagents.

Amongst the polymers prepared from Grignard reagents are:

a. Polyphenylenes from Grignard reagents of dibromobenzene coupled by nickel catalysts [82].

b. Polynaphthylene [82].

c. Head to head polyisobutylene [83].

d. Polymethylene [84].

Organolithium compounds show similar reactions to Grignard reagents except that they are more reactive to alkyl halides. For example Wurtz coupling reactions can be carried out in good yield. One drawback is that they react anionically with conjugated olefins to produce polymers. Also organolithium compounds show nucleophilic substitution reactions on activated aromatics, e.g.phenylpyridine can be made from phenyl lithium and pyridine. A variety of polymers should be available by these routes.

Friedel Crafts reactions.

A large number of polymers have been obtained from Friedel Crafts reactions in addition to those already reported. One area of interest was the production of linear and branched polybenzyls, with or without alkyl side chains.

The synthesis of aralkyl prepolmers by the Friedel Crafts reaction was studied extensively in the 1960´s and early 1970´s. An attempt is currently being made in this laboratory to synthesise water resistant Friedel Crafts polymers using similar reactions. The details are given in Ministry of Defence reports, Contract 2055 / 010 - XR M.T.

Polyphenylenes.

Amongst developments leading to polyphenylene type systems are :

a. Preparation via bis <-2-pyrones > and diethynyl benzenes

[85].
  b. Ketal preparation [32].
  c. Poly ‹dimethyl biphenylene› by a low yield Ullmann reaction [86].
  d. Thermal polymerisation of 4, 4´ diethynyl phenyl ether [20].
  e. Homopolymerisation of benzene to p – polyphenylene via a radical cation initiator, i.e. the reaction of benzene with aluminium trichloride and cupric chloride [87].
  f. Synthesis of polyphenylenes from diethynyl benzenes and tetra substituted cyclopentadienones [88].
  g. Preparation of poly 1,4 phenylene by nickel ‹0› catalysed electropolymerisation [89].

2.5. Summary of potential methods of introducing
unsaturation.

Wittig Reactions.

Besides the example mentioned previously, in which
the Wittig reaction is used both as a polymerisation reaction
and simultaneously as a method of producing unsaturation,
Wittig reactions provide a valuable method by which to modify
prepolymer chains. Any soluble or swellable polymer,
containing chloromethyl or secondary alkyl halide groups,
can be converted into a compound containing a wide variety of
pendant unsaturated groups. The reaction has many advantages
over other routes to such compounds, especially in terms of
specificity, i.e. the position of the double bond is
unambiguous, and high yields are generally obtained. Once the
phosphonium salt is formed, the conditions leading to the
alkene are mild, so the risk of premature polymerisation is
low.
In polymer chemistry the reaction has been used
mainly to functionalise ion exchange resins, by reacting
pendant chloromethyl groups with various aldehydes.
Hodge and Waterhouse [90] obtained 13% functional
yields of pendant vinyl groups on 2% crosslinked
chloromethylated polystyrene by conducting the reaction under
phase transfer conditions with the sodium hydroxide
/dichloromethane /formaldehyde system. Other aldehydes gave
yields of up to 83%.
In a paper concerned with the introduction of
p-oxirane and p-vinyl groups into crosslinked polystyrene,
Frechet and Eichler [91] reported yields of greater than 79%
for a similar reaction to that reported above. The
crosslinked polymer was allowed to swell in aqueous
formaldehyde before treatment with base. A soluble
chloromethylated polystyrene also gave good yields of vinyl
groups by treatment of a dispersion of the phosphonium
polymer in methanol with a base.
The reaction can either be conducted under phase
transfer conditions or by using non aqueous bases such as
sodium ethoxide. Hydrolysis of phosphonium residues should be
reduced by the latter approach.
In this laboratory phase transfer reactions have
been used to modify a chloromethyl terminated polyether with
benzaldehyde and formaldehyde. Formaldehyde produces reactive
(styrene type) unsaturation.These prepolymers, when reacted
with styrene and benzoyl peroxide at 100°C, produced
crosslinked polymers, as did stilbene terminated ethers.
Experimental methods are outlined later.

Dehydration reactions.

In this elimination procedure, alpha substituted aromatic ethyl compounds are dehydrated to styrene derivatives. For example, m- chloro styrene can be obtained in 80% yield by dehydration of the corresponding alcohol [92].

The alcohols are available by a number of routes, including:

a. Formylation and Grignard addition of methyl magnesium iodide. The simple alcohols formed, on dehydration with potassium hydrogen sulphate, gave overall yields as high as 70% [93].

b. Reduction of acetyl compounds.

c. Addition of aromatic Grignard reagents to acetaldehyde (this is a lower yield reaction). Also, analogous beta alcohols can be prepared by the ring opening reaction of aromatic Grignard reagents with epoxides (again low yields).

Decomposition of alpha- hydroxy phosphonates

Acetyl aromatic compounds, readily available via Friedel Crafts reactions, can be converted to styrene derivatives in high yield by the addition of diethyl phosphite. The resultant complex is thermally unstable and yields the alkene on heating. For example, styrene was obtained in 71% yield and stilbene in 81% yield [94].

Organometallic reagents.

It is probably preferable to avoid synthetic methods which are liable to leave residues of water-extractable catalysts in the polymer, if hydrophobic character is important. However, with this reservation, organometallic reagents have the potential to provide several new methods of polymer synthesis.

Grignard reagents are widely known to couple with reactive displaceable halides, such as those in benzylic and allylic halides, often proceeding to good yields. Recent research has shown that a wide variety of compounds can be coupled when transition metals are used as catalysts.

Simple alkyl halides have been coupled by copper catalysts in THF [95] and alkenyl halides have been reacted with simple Grignard reagents to give good yields of unsaturated coupled products [96 - 98]. For example, 1,butene is obtained in 60-70% yields by the reaction of ethyl magnesium bromide with vinyl bromide via iron catalysis.

Other yields were higher.

Unsaturation could conceivably be introduced by:

a. The reaction of unsaturated Grignard reagents with chloromethyl groups.

b. The reaction of aromatic Grignard reagents with allyl bromide.

c. Coupling of aromatic Grignard reagents with vinyl halides, possibly using transition metal catalysts.

Grignard reagents formed from vinyl bromide have been used to functionalise ketone- containing polymers, producing structures containing hydroxyl and vinyl groups in high yields [99].

Aryl Grignard reactions have also been used in a synthesis of a series of p-vinyl oligophenylene oxides via the ring opening of epoxides, the resultant alcohols being dehydrated by potassium hydroxide prior to free radical polymerisation [100].

Aryl lithium compounds show similar coupling reactions with unsaturated alkyl halides, and they could perhaps be used for modification of polymer backbones. Some potential methods of synthesis are:

a. Halogenation, e.g. with bromine and ferric chloride, followed by butyl lithium [101].

b. Mercuration with mercuric trifluoro acetate [102].

c. Direct lithiation with butyl lithium and TMEDA (tetramethyl ethylene diamine) [103].

Also of interest in the field of organometallics is the vinylation of tertiary halides by trivinyl aluminium, and its possible extension to other systems [104].

3. PROPOSED SYNTHETIC PROGRAMME.

It was decided as result of preliminary experiments that two routes were worthy of more attention. These were the Bisphenol A / dichloro p-xylene condensation with Wittig modification [Fig 5], and the synthesis of various unsaturated polymers by the Wittig reaction [Figs 6 and 7].

For the first route the condensation reaction needs to be optimised for yields, and a variety of methods and conditions are possible to achieve this end. The conversion of chloromethyl groups to vinyl groups by the Wittig reaction will also be optimised prior to a study of the crosslinking reaction and the physical properties of the materials produced. A number of variations on the structure of the original backbone are possible.

For the second route the main aim is to produce novel monomers by a variety of means, and then carry out polymerisations.

a. Low molecular weight ethers terminated by chloromethyl groups.

In one procedure, two moles of DCX and 0.02 moles of benzyl triethyl ammonium chloride dissolved in 3:1 mixtures of toluene and DMSO were heated to 60°C under nitrogen, with vigorous stirring. A solution of one mole of Bisphenol A dissolved in 3M KOH was added dropwise to the solution, which resulted in two distinct phases. The reaction was continued for four hours after which time it was acidified with dilute HCl. The aqueous layer was extracted with toluene and the organic portions combined. On removing the solvent with a rotary evaporator, unreacted monomers were removed by washing with methanol. The polymer, obtained in approximately 45% yield was a white powder, soluble in toluene, chloroform etc. The NMR spectrum [see Fig 8] shows peaks at d=7.4 ppm (singlet), d=6.7-7.2 ppm (quartet), d=5 ppm (singlet), d=4.55 ppm (singlet), and d=1.6 ppm (singlet). These can be assigned to aromatic protons from DCX, aromatic protons from BPA, methylene ether protons, chloromethyl protons, and methyl groups respectively. The infra red spectrum shows absorptions characteristic of aromatic/aliphatic ethers, phenyl, alkyl and chloromethyl groups.

b. Conversion of chloromethyl groups to vinyl groups.

A sample of the above polymer and an approximately 2M excess of triphenyl phosphine was heated to reflux in dimethylformamide for three hours under an atmosphere of nitrogen. When the solution had cooled, a concentrated solution of formaldehyde in methanol was added.

The mixture was stirred and cooled, prior to the dropwise addition of a small quantity of 50% aqueous sodium hydroxide. After half an hour the reaction had ceased and the polymer was precipitated with water prior to washing thoroughly with diethyl ether and methanol. The dried polymer, obtained in high yield, was an off white powder soluble in choroform. The NMR spectrum of the compound contained no peak due to chloromethyl protons, but contained new peaks d=5.1-5.9 (quartet) and a series of new peaks in the region d=6-7.5 ppm, which were obscured by the aromatic protons. These new peaks are strongly indicative of styrene type unsaturation.

c. Synthesis of unsaturated prepolymers by the Wittig reaction.

A mixture of equimolar quantities of dichloro p-xylene and dichloro m-xylene was refluxed for six hours with excess triphenyl phosphine in dimethylformamide, to form the phosphonium salts of the two monomers. Terephthaldicarboxaldehyde was added, the temperature was lowered to $0^{O}C$, and a solution of 50% aqueous sodium hydroxide was added dropwise. The reaction was continued for three hours with vigorous stirrring prior to the precipitation of the product in cold water. After filtering, the product was washed with ethanol and dried in the vacuum oven to yield an amorphous yellow powder. Unlike the crystalline product of the Wittig reaction between dichloro p-xylene and the dialdehyde, the new polymer was soluble in dichloromethane, benzene and styrene [see Fig 6].

The polymer was dissolved in styrene and sealed in a tube with a small quantity of benzoyl peroxide. On heating to $150^{O}C$ a highly crosslinked brittle, insoluble material was formed.

The brittleness of the polymer can be attributed to the presence of too many reactive centres on the backbone. In an attempt to modify the above polymer by reducing the density of reactive sites and introducing flexibilising methylene groups, a new monomer has been produced. Fig.7 illustrates this approach in which ditolyl methane is chlorinated under free radical conditions to produce the new monomer. After conversion to the phosphonium salt it was reacted with terephthaldicarboxaldehyde under Wittig conditions to produce an amorphous solid, soluble in dichloromethane, styrene etc. The product softens at $80^{O}C$.

FIG. 5

PREPARATION OF CHLOROMETHYL TERMINATED POLYETHERS AND THEIR
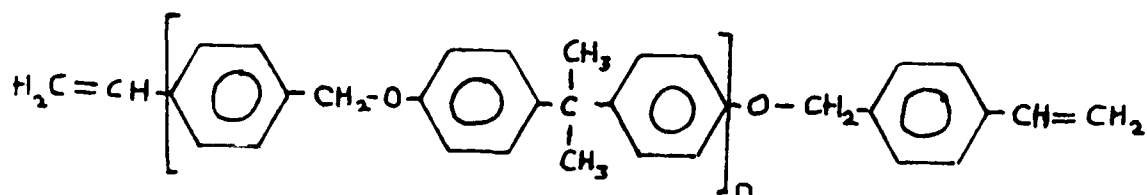CONVERSION TO VINYL DERIVATIVES
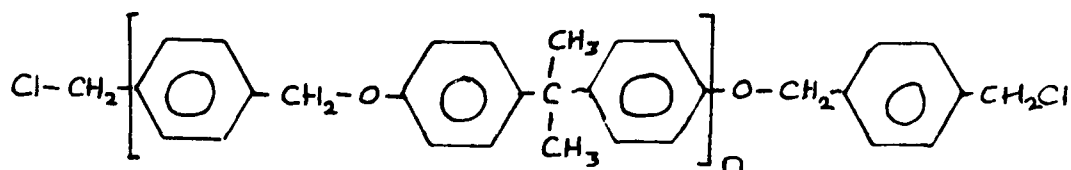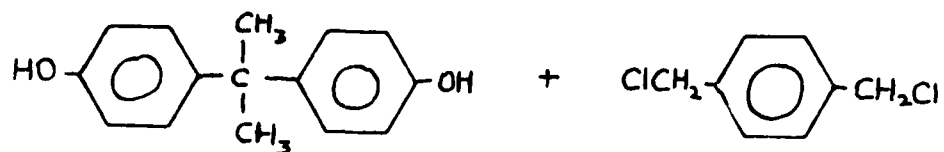
FIG. 6
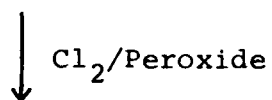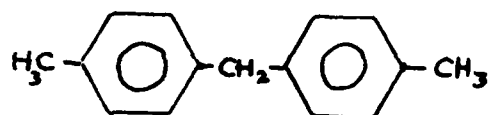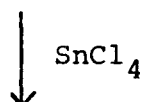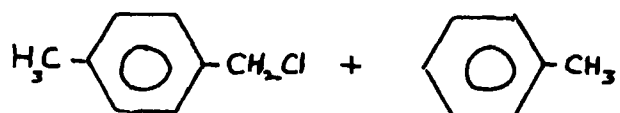
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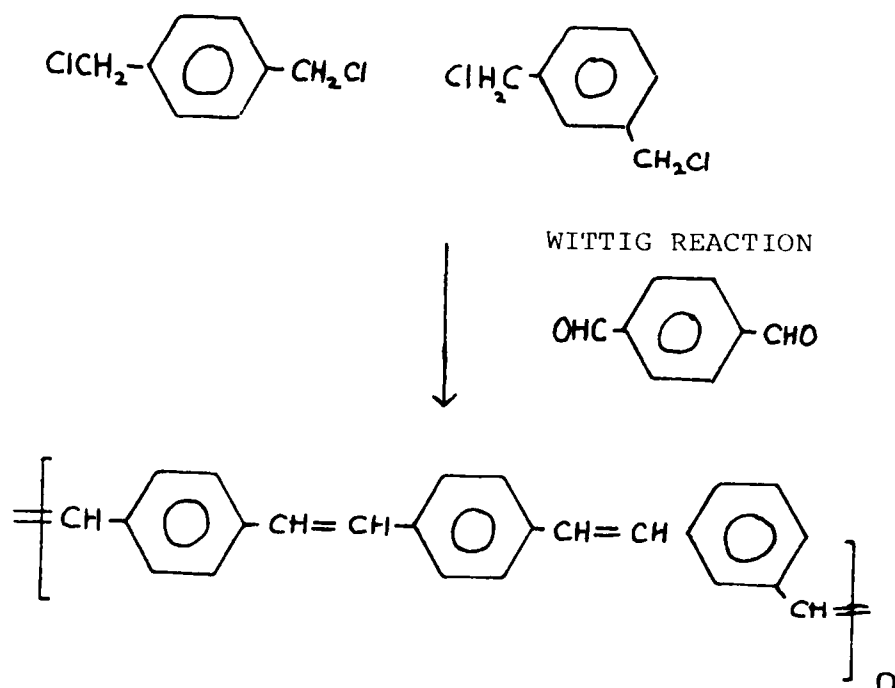
FIG. 7
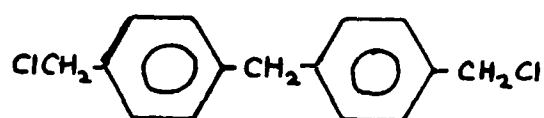
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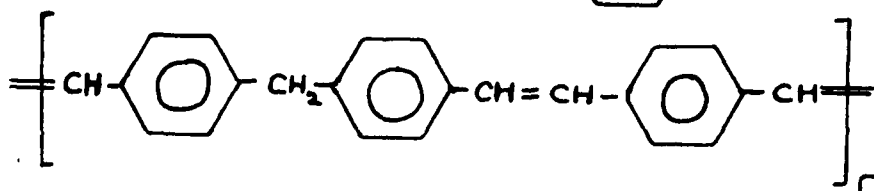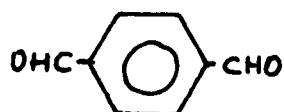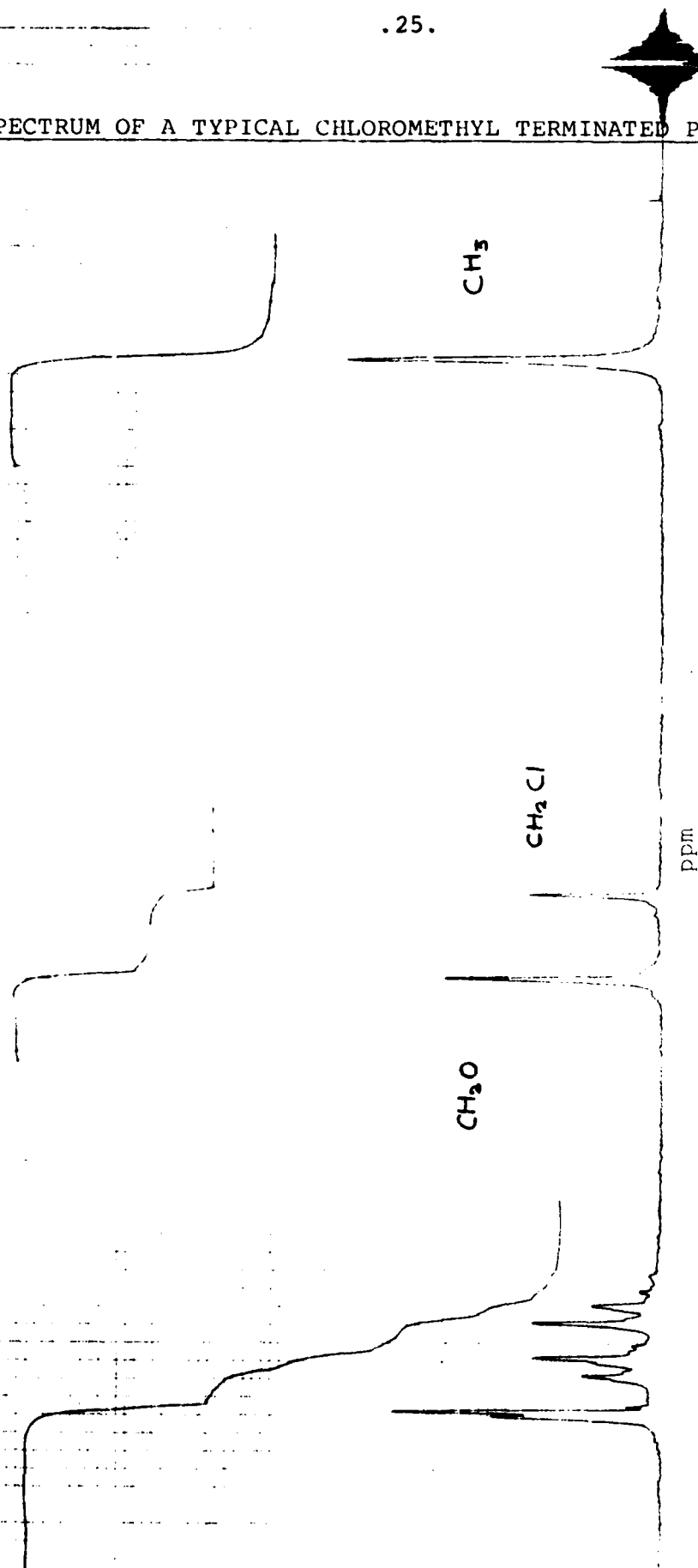
FIG.8

NMR SPECTRUM OF A TYPICAL CHLOROMETHYL TERMINATED POLYETHER

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